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(54) IMPROVEMENTS IN AND RELATING TO THE STORAGE OF HYDROGEN GAS

(71) We, JOHNSON, MATTHEY & CO., LIMITED, a British Company of 43 Hatton Garden, London, EC1N 8EE, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to the storage of hydrogen.

In view of the increasing importance of hydrogen as a source of energy, it is now a frequent requirement to store hydrogen in an accessible form. The conventional method for the storage of hydrogen on a small scale involves the use of thick-walled pressurised cylinders which are weighty and bulky, and in certain circumstances constitute an explosion hazard. On a larger scale it is more convenient to store hydrogen in the liquid state, but this may only be achieved by the use of cryogenic techniques involving expensive liquefaction equipment. It is known that some metals will absorb hydrogen to a lesser or greater extent, resulting in potentially very compact stores, but in most cases the hydrides formed are too stable to be of application as hydrogen storage media.

Certain intermetallic compounds, however, have pressure-composition-temperature relationships which are suitable for the absorption and thus storage of hydrogen, for example as disclosed in British Patent No. 1,291,976.

A limitation in the use of such intermetallic compounds, however, arises from the fact that in addition to the propensity for hydrogen absorption, the hydride forming metal component inevitably forms compounds of high thermodynamic stability with many other gaseous molecules such as O_2, H_2O, N_2, CO and CO_2 etc. The formation of these high stability compounds is an irreversible effect in the hydrogen storage material and in practice results in progressive deterioration or "poisoning" of the store. The source of these poisoning elements is normally from impurities in the hydrogen being stored and these impurities are, from a practical point of view, almost unavoidable in hydrogen obtained from commercial sources. It is, therefore, one object of the present invention to provide an apparatus and method for the storage of hydrogen which may contain impurities.

According to one aspect of the present invention apparatus for the storage of hydrogen comprises at least one membrane constructed from a metallic material containing a major proportion of palladium in gas-tight communication with a gas-tight chamber containing an intermetallic compound capable of reversibly absorbing hydrogen.

According to a second aspect of the present invention a method of storing hydrogen comprises:

(a) causing hydrogen to diffuse through at least one membrane constructed from a metallic material containing a major proportion of palladium, and

(b) contacting the so-diffused gas with an intermetallic compound capable of reversibly absorbing hydrogen.

Preferably, the palladium containing membrane is constructed from pure palladium, 20% by weight silver-palladium or another alloy containing a major proportion by weight of palladium.

The chamber containing the intermetallic compound is, preferably, capable of acting as a heat-exchanger by the provision internally or externally surrounding the chamber, of a heating element and/or heat-exchange tubes for the passage of a heat-exchange fluid.

Examples of intermetallic compounds which are suitable for use in the present invention are $LaNi_5$ which may be used at 1-3 atmospheres pressure and near ambient temperature and TiFe alloys. Another suitable intermetallic compound is Mg_2Ni

operating at 250°C.

The invention will now be described by way of example with reference to the accompanying drawings, in which:-

Figure 1 shows in diagrammatic form, a diffusion and storage apparatus according to the present invention;

Figures 2 and 3 show two different types of diffusion membrane assemblies having a plurality of rectilinear membranes;

Figure 4 is a section through an apparatus according to the present invention utilising tubular membranes; and,

Figure 5 shows an alternative embodiment of the present invention.

In Figure 1 a diffusion membrane 2 made from a palladium alloy is in planar form and is mounted in a vessel V. Impure hydrogen is fed via an inlet pipe 1 to the upstream side of the membrane 2 and waste products are removed via a bleed 3. A storage compound 5 is located in the vessel adjacent to the membrane 2 and a valved outlet 6 is provided for controlling exit of the stored gas. Palladium alloy membranes in such applications will only operate efficiently at elevated temperatures of 150° - 400°C, and it is, therefore, essential to use a storage compound which is compatible with these operating conditions. The titanium-iron materials already mentioned are, consequently, appropriate as also is the compound Mg_2Ni, but the method can equally be applied to any storage substance having the required pressure-composition-relationships with respect to hydrogen.

A heater 4 which may either be external to or housed within the system serves to maintain the diffusion membrane and compound at the operating temperature.

In the diffusion membrane assemblies of Figures 2 and 3, hydrogen from any convenient source is passed under pressure to inlet 1 of a diffusion unit employing a plurality of rectilinear membranes 2 made from palladium, palladium-silver or another alloy of palladium. The ingoing hydrogen-containing gas may be of comparatively low purity and normally completely unacceptable as a hydrogen storage source, for example directly from the catalytic reforming of a hydrocarbon fuel. The hydrogen is separated from this ingoing gas by diffusion through the palladium alloy membranes and issues from the membranes with a very low impurity content, usually a small fraction of one part per million by volume. The impurities or waste products are removed from a "bleed" orifice 3 of the diffusion unit.

The high purity hydrogen issues from the diffusion membranes at a pressure less than the partial pressure of hydrogen in the input gas. Preferably the heater (4 in Figure 1) is in the form of a heat exchange chamber containing intermetallic compound surrounding the diffusion membranes so that the diffused gas is then in contact with the intermetallic compound 5. The chamber will have previously been exposed to high pressure hydrogen or some other activating procedure during its manufacture to ensure that the compound is converted into the activated condition necessary for rapid hydrogen absorption and desorption. Hydrogen will be absorbed by the compound resulting in the well-known exothermic reaction and the heat liberated is removed by the heat-exchanger part of the chamber.

In the diffusion unit of Figure 4 the diffusion membranes 2 of palladium alloy are of tubular form. Impure hydrogen is fed to an inlet 1 fitted with a valve 1A on the upstream side of the membranes and waste products are removed via "bleed" orifice 3 as in the case of the apparatus shown in Figures 2 and 3. The intermetallic storage compound 5 is located in a heat-exchanger chamber adjacent to the tubular membranes 2. A valved outlet 6 for the stored gas is provided as indicated. Palladium alloy membranes in such applications will only operate efficiently at elevated temperatures of, say, 150-500°C, and it is, therefore, essential to use a storage compound which is compatible with these operating conditions. The titanium-iron materials already mentioned previously are consequently appropriate, as also is the compound Mg_2Ni, but the method herein described can equally be applied to any storage substance having the required pressure-composition-relationships with respect to hydrogen. Some form of heater 4/4A which may either be external to or contained in the system is included to maintain the diffusion membrane and the compound at the operating temperature.

When the store is fully charged, the inlet valve 1A is closed and the store is ready for use. When hydrogen is required, the outlet valve 6 is opened. Dehydrogenation of the intermetallic compound is an endothermic process and heat will be supplied as required via the heat-exchange element 4 or tubes 4A. This heat requirement may be employed as a controllable factor in removing hydrogen from the store, only the quantity of heat (conveniently as electrical power) necessary to "boil off" the requisite quantity of hydrogen from the intermetallic compound being supplied at any one time.

When the store is depleted of hydrogen, valved outlet 6 is closed and the cycle repeated. Due to the extremely high purity of the hydrogen stored in the combined diffusion cell-storage vessel system, poisoning effects will be negligible over many cycles and a long operating life for the store will result.

An alternative embodiment of the present invention is illustrated in Figure 5. The storage intermetallic compound 5 is contained in

a multiplicity of thin-walled palladium alloy containers 2A. These may be formed from palladium - 23% silver foil 0.002 in. thick, folded and welded on three sides to form small "ravioli-like" units or envelopes shown encircled in Figure 5. Alternative units may equally well be formed by other means such as packing the compound into thin-walled tubes, or vapour depositing or plating the palladium base envelope onto the storage medium, provided the compound is physically separated by the hydrogen permeable membrane from the impure gas. In operation of the apparatus, the hydrogen from a source is supplied to the vessel V via inlet 1 and waste products removed via a valved "bleed" 3. For discharging the store the source should be disconnected, and the hydrogen passed via valved outlet valve 6 to a user. In this embodiment, during the discharge cycle it is necessary for the hydrogen to be desorbed by the intermetallic compound and subsequently, permeate in a reverse direction through the thin palladium alloy walls or membranes before being available at the outlet 6. Heating is provided as previously described at 4. It is further desirable that the upstream volume or volume not filled with encapsulated compound be kept to a minimum in the unit shown in Figure 5 to ensure that any impurity carryover in the issuing gas is also kept to a minimum. Alternatively, this free volume may be purged with pure hydrogen before attempting to discharge the store.

WHAT WE CLAIM IS:-

1. Apparatus for the storage of hydrogen comprising at least one membrane constructed from a metallic material containing a major proportion of palladium in gas-tight communication with a gas-tight chamber containing an intermetallic compound capable of reversibly absorbing hydrogen.

2. Apparatus according to Claim 1, wherein the said chamber has heat exchange means for removing the heat liberated when the hydrogen is absorbed by the intermetallic compound.

3. Apparatus according to Claim 1 or Claim 2 wherein the metallic material is palladium or an alloy consisting essentially of 20 wt % silver and balance palladium.

4. Apparatus according to any one of Claims 1 to 3, wherein the intermetallic compound is $LaNi_5$, TiFe alloy, or Mg_2Ni.

5. Apparatus according to any one of Claims 1 to 4, wherein the said chamber includes heating means for applying heat to the intermetallic compound and the membrane.

6. Apparatus according to Claim 5, wherein the heating means is located internally or externally relative to the chamber.

7. Apparatus according to any one of Claims 1 to 6, wherein the membranes are formed into rectilinear envelopes.

8. Apparatus according to any one of Claims 1 to 6, wherein the membranes are formed into tubes.

9. A method of storing hydrogen comprising

(a) causing hydrogen to diffuse through at least one membrane constructed from a metallic material containing a major proportion of palladium, and

(b) contacting the so-diffused gas with an intermetallic compound capable of reversibly absorbing hydrogen.

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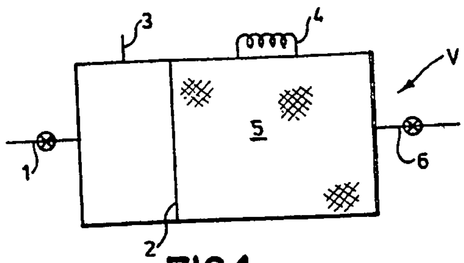

FIG.1.

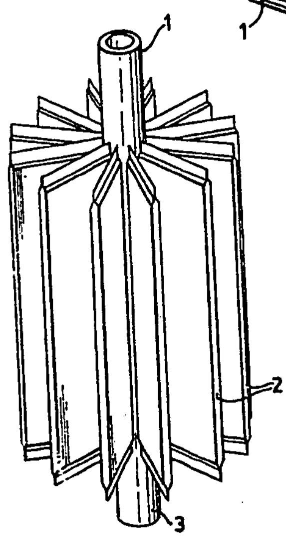

FIG.2.

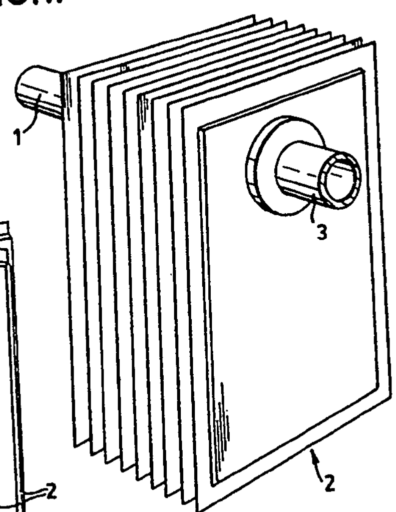

FIG.3.

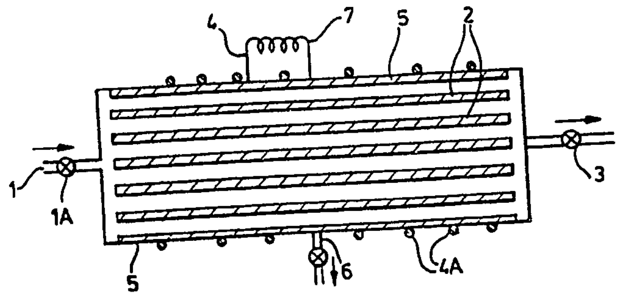

FIG.4.

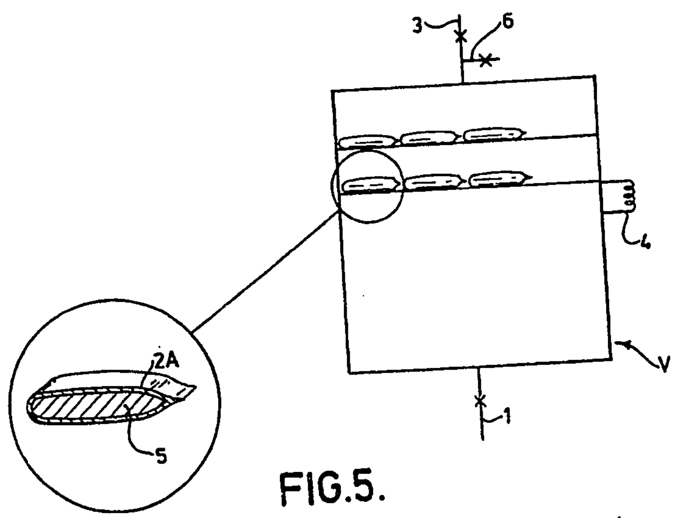

FIG.5.